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14/

Claim (s)

Abstract

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Organic-inorganic hybrid transistors

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This invention relates to a new class of organic-inorganic hybrid materials for thin film transistors that exhibit good stability in water, as well as processing of such transistor device and the reduction of impurities by exposure to water.

Semiconducting conjugated polymer field-effect transistors (FETs) have potential applications as key elements of integrated logic circuits (C. Drury, et al., APL 73, 108 (1998)) and optoelectronic devices (H. Sirringhaus, et al., Science 280, 1741 (1998)) based on solution processing on flexible plastic substrates. One main criterion to obtain high charge carrier mobilities has been found to be a high degree of structural order in the active semiconducting polymer.

Local order in thin polymer films can be achieved by making use of the tendency of some polymers to self-organise. An example is poly-3-hexylthiophene (P3HT) in which microcrystalline, lamelia-type ordered structures can be formed by phase segregation of rigid main chains and flexible side chains. By using suitable deposition techniques and chemical modification of the substrate it is possible to induce preferential orientations of the ordered domains of the polymer with respect to the substrate surface. At present P3HT yields the highest known field-effect mobilities of 0.05-0.1 cm²/Vs for polymer FETs (H. Sirringhaus, et al., Science 280, 1741 (1998)). In these known devices there is no preferential, uniaxial alignment of the polymer chains in the plane of the film. The high mobilities are due to efficient interchain charge transport along the direction of close π - π stacking in the plane of the conjugated lamellac.



Realization of the often-made promise and much-heralded announcements of mass-produced, low-cost "plastic electronics" based on semi-conducting organic materials (Heeger, A. J., Rev. Mod. Phys. 73 (3), 681-700 (2001)) requires, among other qualities, ease of processing, and, more importantly, stability during fabrication and practical use of the final products. Virtually all organic polymers and oligomers that are under current scrutiny for this purpose appear to suffer from degradation upon exposure to oxygen and water, and, hence, require manufacturing conditions, as well as packaging systems such as glass, that are prone to eliminate at least some of their purported benefits.

According to a first aspect of the present invantion we disclose a new class of solution processible semiconducting materials for thin film transistor applications that exhibit extraordinary stability when washed in water for prolonged periods of time at elevated temperatures. The materials comprise semi-conducting, metal-based chain-structures such as those comprising Pt, Pd, and others or mixtures thereof, synthesized in, for instance, aqueous media substituted with organic ligands.

It is envisaged that the ligands may be the same of different at all occurrences, and that the ligands may display at least one or more of the following functions or characteristics: i.) promote solubility; ii.) be capable of forming a covalent bond with another ligand, for instance upon irradiation; iii.) display photoluminescence or other functional optical properties; iv.) be an electron-accepting (n-type) or electron-donating (p-type) semiconductor.

Thin films were produced under ambient conditions from common organic solvents, and exposed -without significant loss of performance- to white light and air for periods of time in excess of 6 months. Remarkably, immersion of the FETs in water of 90 °C for more than 12 hrs did not deteriorate important device characteristics, but, in fact improved, for instance, their ON-OFF switching ratios by a factor 10 and more.

According to a second aspect of the present invention a technique is disclosed that allows to reduce the level of impurities and residual dopants in a thin film semiconductor device that contains impurities, for instance ionic species. The technique is based on washing the as-deposited film or completed device in deionised water. After washing a reduction of the bulk film conductivity, i.e. the impurity concentration, and a reduction in device hysteresis without significant degradation of the charge carrier mobility is be achieved.

The invention will now be described with reference to the following figures:

Figure 1 a. Schematic of the chemical structure of solution-processible, semi-conducting tetrakis((S)-1-amino-3,7-dimethyloctane) platimum(II)- tetrachloroplatinate (II), [Pt(NH₂dmoc)₄][PtCl₄]. b. Wide-angle X-ray diffraction patterns recorded (from 20 = 10°) at the various temperatures indicated. In this dynamic experiment, the crystalline order in the Pt-compound was observed to irreversibly disappear at ~140°C.

Figure 2 a. Polarized optical micrograph of an oriented filament of [Pt(NH2dmoc)4][PtCl4] produced by electro-spinning¹⁵ from a super-cooled, viscous 45 % w/w solution in toluene. Portions of the filaments that appear dark in the image are parallel to the (crossed) polarizer or analyzer. b-d. Films of an extraordinary degree of uniaxial crystalline order of [Pt(NH2dmoc)4][PtCl4] could readily be grown under ambient conditions from, for instance, a 2 % w/w, supersaturated solution in toluene onto a glass substrate that was coated with an ultra-thin layer of friction-deposited poly(tetrafinoroethylene). b. Electron diffraction pattern revealing the orientation of the Pt-compound along the PTFE macromolecules (arrow). The open circle marks the faint reflection of the 0.1294 nm spacing along the PTFE chains. c,d. Scanning probe microscopy images revealing the very high degree of uniaxial order in the films and

suggestive of the helical nature of [Pt(NH2dmoc)4][PtCl4] possibly induced by the chiral ligand (S)-3,7-dimethyloctyl-1-amine. c. Original image taken in deflection mode; inset: fast-Fourier transform (FFT). d. FFT-filtered image of e; inset: FFT-filtered height image.

Figure 3 a. UV-vis (dotted grey curve) and circular dichroism spectrum (solid curve) of a 1 µm film of the green Pt-compound cast from toluene. The weaker absorption band at longer wavelengths is responsible for the green color, and is attributed to localized Pt d-d transitions. b. The transient change in conductivity, Ac, on irradiation of [Pt(NH2dmoc)4][PtCl4] with a 10 ns pulse of 3 McV electrons detected by time-resolved microwave conductivity at a frequency of 33.5 GHz. The conductivity is normalised to the energy deposited in the sample, A J/cm³.

Figure 4 a,b. Optical micrograph (a) and schematic representation (b) of a thin-film field-effect transistor (FET), produced under ambient conditions, comprising [Pt(NH2dmoc)4][PtCl4] (aligned on highly-oriented PTFE (3)) as the active semiconducting layer (4), vacuum-evaporated gold source/drain electrodes (5), and an n++ doped silicon wafer (I) with a 200-nm thin oxide layer (2) as gate and gate insulator, respectively (channel length, $L=70~\mu m$; width, W=1.5~mm; insulator capacitance, C_i = 16 nF/cm²). c. Transfer characteristic of as-produced device. d. Characteristic of the same device, but stored for 12 hrs in water at 80 °C. (Insets: Corresponding logarithmic plots.) e. Output characteristics of [hot-]water-treated FETs, comprising highly oriented (graph) and spin-coated, unoriented (inset) [Pt(NH2dmoc)4][PtCl4] active layers. f. Relationship of field-effect mobility, µFET, and conductivity, q as determined from FET device characteristics. owas derived from the output characteristics:

$$\sigma = \frac{L}{W t} \cdot \frac{I_{ed}(V_g = 0V)}{V_{ed}}$$

with t, the thickness of active, semi-conducting layer. Squares and triangles represent data taken for FETs based on aligned [Pt(NH₂dmoc)₄][PtCl₄], channel parallel to Ptchains; open squares, as-prepared devices; solid black symbols, devices of different batches after various temperature and kinetic studies, but before H₂O-bath; solid blue symbols, devices after hot-water treatment. Open black circles are data points for devices with channel perpendicular to chains, before water storage; open blue circle: spin-coated device, after water treatment. For comparison, the power-law relationship collected by Brown et al. [Brown, et al., Synthetic Metals 68, 65-70 (1994)] for various amorphous organic semi-conductor FETs is also included.

Organic-inorganic hybrid materials recently have been proposed as possible alternatives to organic semi-conductors. Indeed, a number of interesting electronic devices have been demonstrated with materials such as those based on intercalated organic tin(II)iodide perovskites (Kagan, C. R., Mitzi, D. B. & Dimitrakopoulos, C. D., Science 286, 945-947 (1999); Chondroudis, K. & Mitzi, D. B., Chem. Mater. 11, 3028-3030 (1999)). Despite the beneficial fact that the synthesis of these materials may be carried out under convenient hydrothermal conditions, unfortunately, also these materials appear to suffer from environmental instability, manifested, for instance, in the form of deintercalation — a process that may occur already at room temperature (Mitzi, D. B., Medeiros, D. R. & Malenfant, P. R. L., Inorg. Chem. 41, 2134-2145 (2002)).

Unlike the layered organic-inorganic hybrid materials mentioned above, the semi-conducting material in the present work is a quasi-one dimensional chain-structure with a backbone of, for instance, linearly arranged platinum atoms (Fig. 1a). This embodiment is based on Magnus' green salt, [Pt(NH₃)₄][PtCl₄], that was described as long ago as 1828 (Magnus, G., Pogg. Ann. 14, 239-242 (1828)), for an excellent overview see Interrante, I. V., Adv. Chem. Ser. 150, 1-17 (1976). The original salt and many subsequently produced modifications thereof are characterized by a Pt-Pt distance

that typically is between 0.32-0.36 nm, depending on the derivative, as opposed to 0.277 nm in platinum metal. Unfortunately, these early Pt-compounds are virtually intractable and, as a result, have found no practical applications. However, by carefully selecting the chemical structure of the ligands, e.g. NH₂R with R a linear or branched alkyl group, in analogy to imparting tractability to, for instance, polyaniline, it has proven possible to synthesize soluble [Pt(NH₂R)₄][PtCl₄] compounds. These have been shown to exhibit a polymeric, quasi-linear Pt-chain structure even in solution and can actually be better represented as ([Pt(NH₂R)₄][PtCl₄])_a; with n varying between about 10 and 1,000, depending on the particular alkyl substituent (Bremi, I., Caseri, W. & Smith, P., I. Mater. Chem. 11, 2593-2596 (2001); Fontana, M. et al., Chem. Mat. 14, 1730-1735 (2002)). As shown here, particularly beneficial properties are found for the derivative in which R is (S)-3,7-dimethyloctyl (dmoc).

Synthesis of compounds of the type [Pt(NH2R)4][PtCl4], which is one embodiment of the present invention, is simple in that it requires none of the special environments or particular precautions, such as exclusion of air and water, often encountered for the synthesis of popular organic semi-conductors. The procedure comprises dissolving K2[PtCl4] in water, to which the selected amino-compound is added (here (S)-3,7-dimethyloctyl-1-amine) and, subsequently, another equimolar quantity of K2[PtCi4], yielding the desired compound. The product is extracted from the reaction mixture simply dissolution ìn, for instance, hot [Pt(NH2dmoc)4][PtCl4] thus obtained is a green, crystalline material that is thermally stable in air up to above 130 °C (Fig. 1b).

[Pt(NH₂dmoc)₄][PtCl₄] is highly soluble at moderately elevated temperatures (-70-80 °C) in a variety of common organic solvents, including toluene, trichloroethane, p-dichlorobenzene and xylene, from which the Pt-compound can conveniently be recrystallized by cooling or evaporation of the solvent under ambient

conditions. This very desirable property makes it possible to readily form films, fibers (Fig. 2a), blends with polymers, and other structures. Also, the growth of highly oriented films of [Pt(NH₂dmoc)₄][PtCl₄] was found to be a rather trivial exercise. When glass slides covered with a friction-deposited transfer film of poly(tetrafluoroethylene) (PTFE) were introduced as orienting substrate into a super-saturated toluene solution of the Pt-compound, it crystallized in the form of a film of an extraordinary high degree of uniaxial orientation along the axis of the PTFE macromolecules. From the very rich electron diffraction patterns of such films (Fig. 2b) the Pt-Pt distance was determined to be 0.31 mm, which is shorter than the spacing found in previously synthesized members of the [Pt(NH₂R)₄][PtCl₄] series and is closer to that in Pt metal. Spin-coating under ambient conditions yielded relatively amorphous films, as evidenced by polarizing optical microscopy and X-ray analysis, due to the low rate at which the complex process of self-ordering of the linear Pt-chains takes place.

UV-vis spectra of $[Pt(NH_2dmoc)_4][PtCl_4]$ films (Fig. 3a) were dominated by an absorption maximum at a wavelength $\lambda = 310$ nm that was previously assigned to a $5d_{2^2}$ - $6p_x$ charge-transfer transition from the $[PtCl_4]^2$ to the $[Pt(NH_2R)_4]^{2+}$ unit. The films displayed a distinct bisignate Cotton effect, indicative of strong excitonic coupling between the chromophores. Ultra-high chiral anisotropy factors g_{abs} (= $\Delta e/e$ of the same film at the same wavelength) of -0.11 and 0.10 were determined for the first and second Cotton effect at $\lambda = 314$ and 298 mm, respectively. These values exceed those usually found for organometallic and organic substances, including certain biomolecules that were reported to exhibit "giant" circular dichnoism.

The bulk electrical conductivity at room temperature of compacted powder pellets of [Pt(NH₂dmoc)₄][PtCl₄] was 2.10⁻⁷ S/cm, which is in the range of 10⁻⁶ -10⁻⁸ S/cm reported previously for many other quasi-one dimensional metal compounds, e.g. iridium, gold, nickel, and platinum complexes including Magnus' green salt itself

(Miller, J. S. & Epstein, A. J., Prog. Inorg. Chem. 20, 1-151 (1976); Rao, C. N. R. & Bhat, S. N., Inorg. Nucl. Lett. 5, 531-532 (1969)). (It should be noted that the electrical conductivity of Magnus' green salt can be significantly influenced by the presence of impurities (Mehran, F. & Interrante, L. V., Solid State Commun. 18, 1031-1034 (1976)). Reduction of the conductivity values of about a factor of 10 were recorded upon treatment of the material for 12 brs in H₂O at 90 °C.

The intrinsic mobility of charge carriers in [Pt(NH2dmoc)4][PtCl4] has been determined using the pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC) (Schouten, P.G., Warman, J.M. & de Haas, M.P., J. Phys. Chem. 97, 9863-9870 (1993)). From the room temperature, transient radiation-induced conductivity shown in Fig. 3b, the one-dimensional mobility along the Pt-chains is determined to be ≥ 0.06 cm²/Vs. This compares favorably with values found for πstacked discotic materials and π-bond conjugated polymers using the same technique. The mobility determined by PR-TRMC is the trap-free value and is expected to be close to the optimum value that could be achieved in a DC device structure for a wellorganized layer of the semi-conductor material between the electrodes. This has been shown to be the case for time-of-flight measurements on the discotic material α,ω FET measurements onhexakis(hexylthio)triphenylene and for dihexylquaterthiophene. Well-aligned, defect free layers of [Pt(NH2dmoc)4][PtCl4] should, therefore, ultimately be capable of sustaining current densities and switching times comparable with the best molecular semi-conductor materials presently in use or proposed.

Simple, field-effect transistors comprising [Pt(NH2dmoc)4][PtCl4] as the active semi-conductor layer were produced under ambient conditions in air both with highly oriented films grown onto PTFE orientation layers and isotropic, spin-coated films of the Pt compound (Fig. 4). Devices in which the Pt-chain structures were aligned parallel

to the current transport direction exhibited p-type transistor action with field-effect mobilities on the order of 10^{-3} - 10^{-4} cm²/Vs. We attribute this to injection of holes into the valence band which is based on the Pt d_z² orbitals and is therefore delocalized along the polymer axis. In contrast, we were not able to obtain n-type operation. The observation of clean transistor device operation in this material is remarkable as it demonstrates that the level of mobile ionic impurities in [Pt(NH₂dmoc)₄][PtCl₄] is sufficiently low that the formation of an accumulation layer of field-induced charge carriers at the active semi-conductor/dielectric interface is possible. [Pt(RNH₂)₄][PtCl₄] compounds are a new class of organic-inorganic hybrid materials for thin film transistors.

In as-prepared devices a relatively high film (bulk) conductivity on the order of 10⁻⁷ S/cm was observed (Fig. 4c and f), limiting the ON-OFF current ratio of the transistors to less than 10 (inset in Fig. 4c). Unpackaged transistors were immersed in water at a temperature of up to 90 °C for a period of 12 hrs and more, followed by drying under vacuum for 12 hrs. For selected samples, this procedure was repeated twice. Afterwards a decrease of the film conductivity by more than one order of magnitude was observed resulting in an increase of the ON-OFF current ration to $>10^2$. 103 (inset Fig. 4d) and suggesting a removal of impurities, such as ionic species, by the water "washing". In addition the hysteresis of the device characteristics between subsequent sweeps of the gate/source-drain voltage was significantly reduced. Most remarkably, the transistor devices showed no evidence of degradation demonstrating the extraordinary stability of [Pt(NH2dmoc)4][PtCl4] (Fig. 4d,e). A small decrease of the field-effect mobility was noted upon water exposure, which is explained by a direct relationship between the field-effect inobility μ FBT and the film conductivity σ of the form $\mu_{\text{PET}} \propto \sigma^{\alpha}$ ($\alpha \approx 0.7$) (Fig. 4f). A similar relationship had previously been observed for doped, amorphous conjugated polymer semi-conductors²⁸ in which an increase of dopant concentration, i.e., bulk conductivity, enhances the hopping rate between transport

sites. The small observed reduction in mobility is therefore not a sign of material degradation, but is entirely consistent with the reduction in film conductivity. It also indicates that, in contrast to the more unicroscopic PR-TRMC measurements, the mobility observed in FET devices is still limited by transport in disordered regions of the film, presumably grain boundaries.

Mobilities obtained for devices produced with the channel perpendicular to the oriented [Pt(NH₂dmoc)₄][PtCl₄] molecules and for those devices produced by spin-coating of an isotropic active layer onto Si/SiO₂ wafers void of PTFE orientation layers, were found to be two and three orders of magnitude lower than the above values, respectively (cf. inset Fig. 4e). This finding once again illustrates the importance of acquiring control of the structural order in the active semi-conductor layer, which is readily achieved for this Pt-chain compound.

The observation of improvement of transistor characteristics after "water washing" shows that the water treatment reduces the concentration of impurities and unintentional dopant atoms. We believe that this procedure is advantageous also for other semiconductors, where ionic impurities affect the device performance. One of the requirements for successful washing purification is a good stability and insolubility of the as-deposited semiconducting material and other layers of the device in water as well as good adhesion of the different layers of the device in order to prevent delamination during the washing step.

Many technological applications of solution-based thin film transistors such as integrated logic circuits and active-matrix displays require mobilities of 10⁻³-10⁻² cm²/Vs or higher and ON-OFF current ratios exceeding 10⁵ which have been achieved in devices comprising organic semi-conducting polymers such as poly(3-hexylthiophene) or polyfluorene derivatives (e.g., poly(fluorine-co-bithiophene)

[Sirringhaus, H. et al., Appl. Phys. Lett. 77, 406-408 (2000)]. Under optimized conditions, the latter are reported to display mobilities up to 0.1 cm²/Vs and 0.02 cm²/Vs, respectively. The PR-TRMC for the intrinsic mobility for the Pt-compound imply that further improvements in device performance may be achieved by, for example, additional purification, ordering of the present material and optimization of the device design. The extraordinarily simple and versatile synthesis (which permits easy incorporation of additional functionalities), convenient processibility, and outstanding resistance to relatively harsh environmental conditions, combined with the not-prohibitive cost of the principal starting material (estimated to be about one-fifth of that of substituted poly(phenylene vinylenes) and pentacene), could make compounds of the type of the present [Pt(NH₂dmoc)₄][PtCl₄] the material of choice for certain "sloppy" electronic products

In the following a detailed description of materials, thin film and device preparation as well as film characterization is given.

A detailed description of the synthesis of [Pt(NH2dmoc)4][PtCl4] was previously presented [Fontana, M. et al., Chem. Mat. 14, 1730-1735 (2002)].

Time-resolved, variable temperature wide-angle X-ray scattering (WAXS) experiments were performed on the BM26B DUBBLE beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The data were collected with a curved micro-strip gas chamber detector positioned such that its center of curvature coincided with the sample position, and in time frames of 10 s. Reflections of the α-phase of isotactic polypropylene recorded at a wavelength of 0.154 nm were used to calibrate the detector. [Pt(NH2dmoc)4][PtCl4] powder was sandwiched between mica sheets and enclosed in a small aluminum sample holder (used for differential scanning calorimetry), which was placed in a modified Linkam THMS 600 hot-stage equipped with a TMS-92 controller, A heating rate of 5°C/min was used. Optical microscopy was

carried out with a Leica DMRX polarizing microscope, equipped with a Mettler Toledo FP82 HT hot stage. Transmission electron microscopy (TEM) was performed with a Philips CM300 instrument operated at 200 kV under low-dose conditions selected to avoid reduction of the Pt-compounds to elemental platinum. Scanning probe microscope images were recorded in air in the contact mode with a Nanoscope E instrument (Digital Instruments, Santa Barbara, Calif.), which was calibrated with muskovite mica. UV-vis spectroscopy and circular dichroism measurements were carried out on films of a thickness of about 1 µm cast onto quartz glass; a Perkin Elmer Lambda 900 instrument and Jasco J-600 spectropolarimeter were employed. Bulk conductivities were measured on pressed pellets by determining the DC resistance with two contacts clamped on each side of pressed pellets of 2 mm (hickness and 10 mm diameter.

Thin films of [Pt(NH2dmoc)4][PtCl4] were generally prepared by casting or spin-coating (500 rpm, 300 s (Fairschield Technologies 1001)), from solutions comprising, resp. 0.2 and 2.0 % w/w of the compound in toluene, and which were prepared by heating at 80 °C for 30 min after which a clear, green solution was obtained. Oriented growth of films of the Pt-compound was effectuated by immersing a glass substrate coated with a friction-deposited, thin layer of FTFE [Wittmann, J.-C. et al. Nature 352, 414-417 (1991)] at room temperature into a super-saturated solution of the material, prepared by % w/w of [Pt(NH2dmoc)4][PtCl4] in toluene at 80 °C. After dissolving 0.2 approximately 2 hrs, a film of a thickness of about 100 nm had formed, remarkably, solely onto the PTFE-coated area. Electrostatic-spinning was carried out according to standard techniques by applying a voltage of 10 kV over an electrode immersed into a capillary containing a hot 45 % w/w solution of [Pt(NH2dmoc)4][PtCl4] in toluene and a ground plate, resulting in moderately oriented filaments of the Pt-compound of lengths up to 5 mm and cross-sectional dimensions in the range from 0.1- 2 µm. One set of field-effect transistors **Was** assembled depositing thin, aligned [Pt(NH2dmoc)4][PtCl4] films on PTFE-coated Si(n++)/SiO2 waters. Two gold, chargeinjecting ohmic source-drain contacts were evaporated on top of the semi-conducting film using a shadow mask. For comparison, another set of devices comprising spincoated films was fabricated from a 2 % w/w toluene solution. All device characteristics were determined with a semi-conductor parameter analyzer HP 4145B at room temperature. Charge carrier mobilities μ_{FBT} were extracted from the respective transfer characteristics (Fig. 4c,d) employing the relation:

$$\frac{\delta \mathbf{I}_{sd}(V_g)}{\delta V_g} = \frac{C_i \cdot W}{L} \mu_{FET}(V_g, V_{sd}) \cdot (V_g - V_0)$$
(1).

where Isd is the source-drain current (saturation regime), Vg and Vsd gate and source-drain voltage, respectively, Ci, the insulator capacitance, W and L the channel width and length, and, Vo, the turn-on voltage (see inset Fig. 4d).

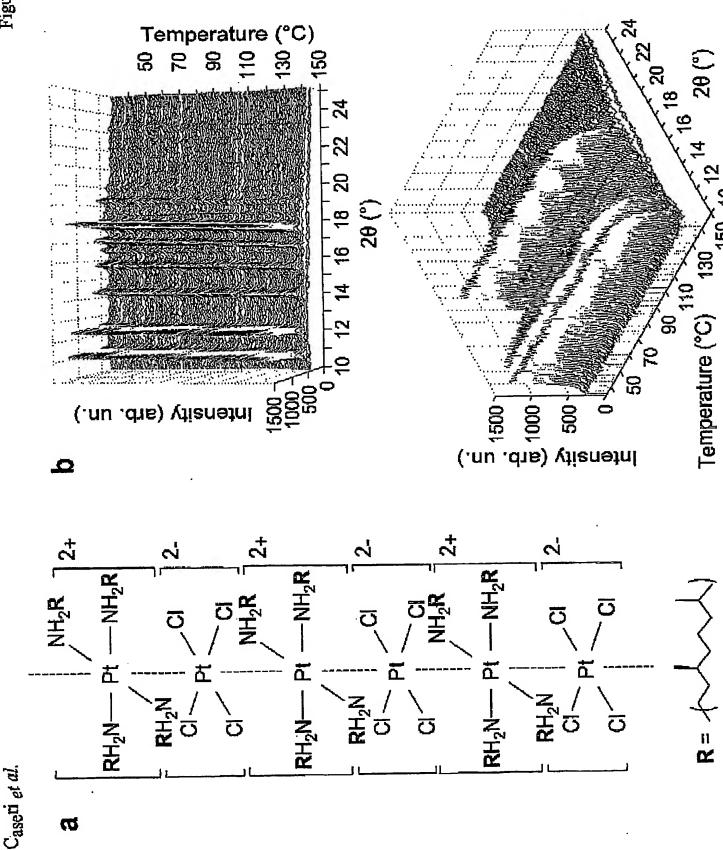
The new class of thin film organic-inorganic semiconducting devices, as well as the purification technique for thin film semiconducting devices containing impurities, such as ionic species, according to this invention are useful in the context of TFT logic circuits (C. Drury, et al., APL 73, 108 (1998)) or pixel drive transistors in highresolution, active matrix displays (H. Sirringhaus, et al., Science 280, 1741 (1998)). Examples of such displays are active matrix polymer LED displays, liquid-crystal displays (LCD) or electrophoretic displays. The invention can also be used for the fabrication of other thin film semiconducting devices such as rectifying diodes, light emitting diodes, or photovoltaic diodes.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof, irrespective of whether it relates to the presently claimed invention. In view of the foregoing

description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

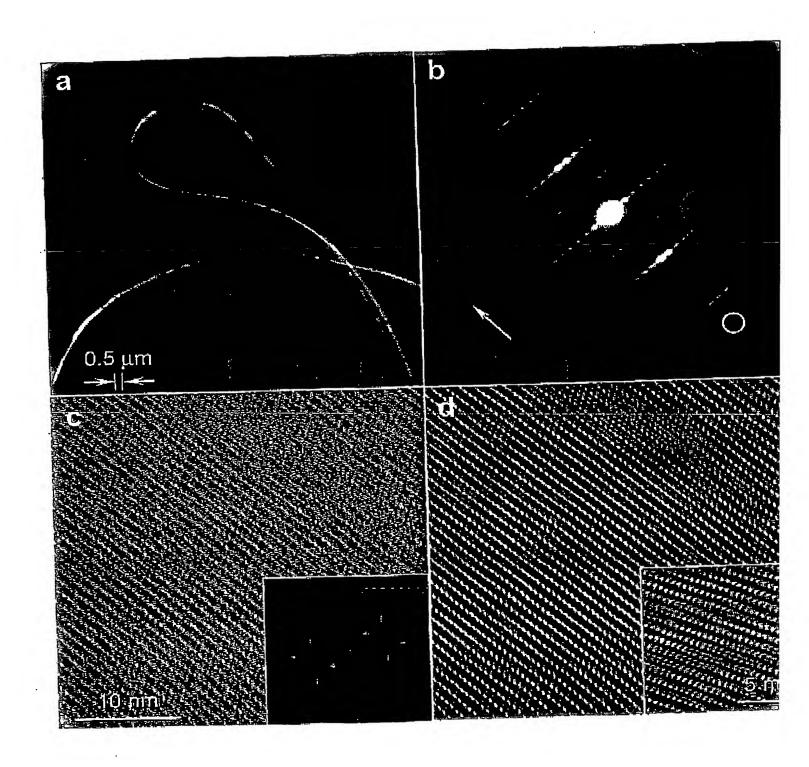
Organic-inorganic hybrid transistors

A new class of organic-inorganic materials for thin film semiconducting devices that exhibit good stability in air and water, as well as a new purification technique for thin film semiconducting devices that contain impurities, such as ionic species.



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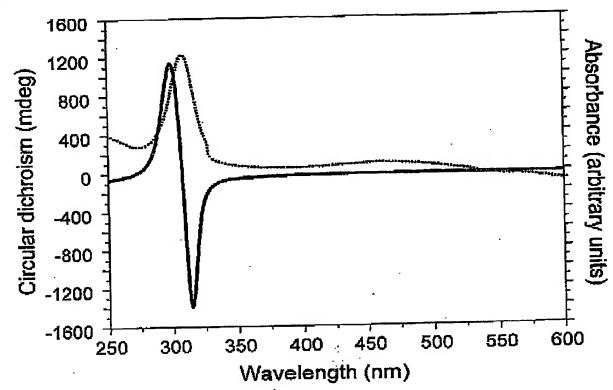
Figure 2



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Figure 3





b

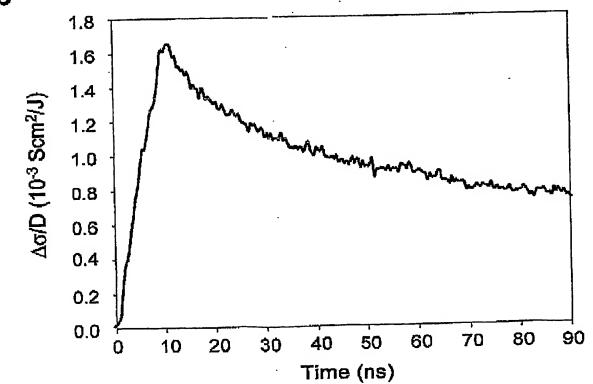
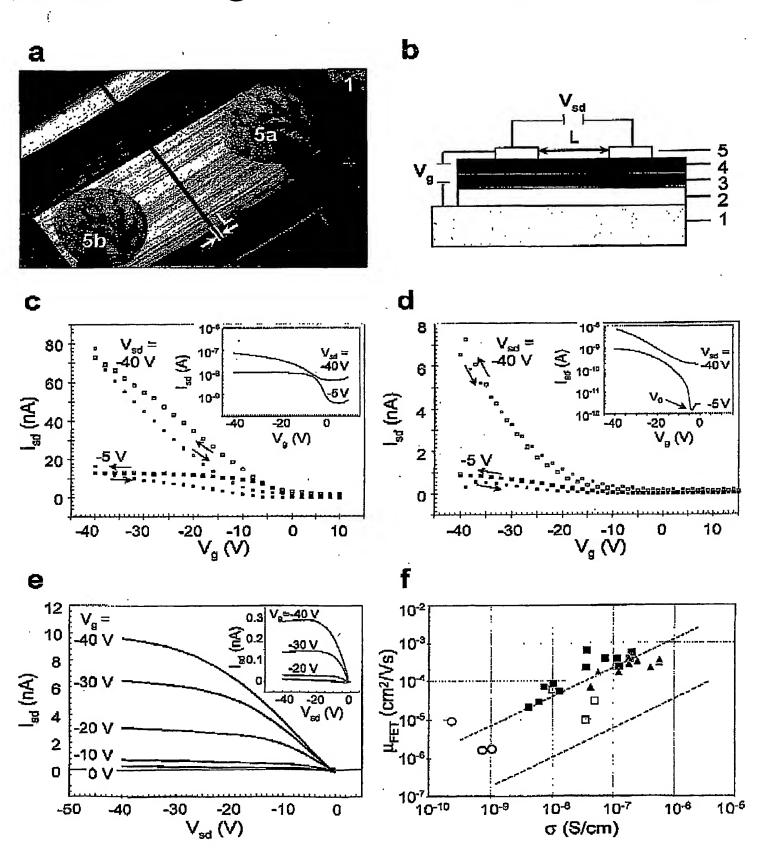


Figure 4



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